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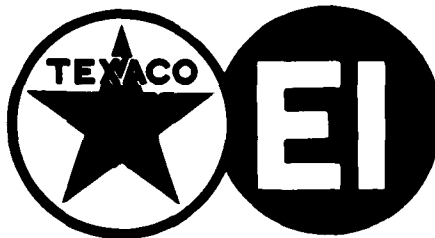
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TEXACO
EXPERIMENT INCORPORATED

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COMBUSTION OF ELEMENTAL BORON

**Quarterly Summary Report for
November 1961 through January 1962**

TM-1326

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SUMMARY

Our earlier observation that boron monofluoride, BF, is the species evolved from the surface of a heated boron rod exposed to fluorine gas inside a mass spectrometer has been confirmed. Evidence also is presented that the rate of formation of BF is only slightly dependent on temperature above 1200°K.

Preliminary experiments in a microbalance apparatus show no detectable reaction between a high-purity polycrystalline boron rod at ambient temperature and fluorine gas at 1 to 200 μ Hg pressure. However, a boron rod heated to about 600°K in an image furnace gives a reaction rate of about 10^{16} molecules/cm²-sec at a fluorine pressure of 1 μ Hg. This value is subject to an upward revision since it corresponds to approximately total consumption of the fluorine at the flow rates possible with the equipment.

INTRODUCTION

Research on this contract has been concerned with investigating the combustion of elemental boron with various oxidizers to obtain a better understanding of this phenomenon. Results of research done on the combustion of boron with oxygen are given in references 1 through 3. Recently work has begun on the study of the combustion of boron with halogen oxidizers (4, 5). This report covers work done during the period November 1961 through January 1962.

OXIDATION OF BORON WITH FLUORINE IN THE MASS SPECTROMETER

Experiments run in a Bendix Time-of-flight Mass Spectrometer (Figures 1 and 2) indicate that there is apparently no reaction between BF_3 and a heated high-purity polycrystalline boron rod. The inlet system for the mass spectrometer in which these experiments were performed is described in reference 4b. As can be seen from the results given in Tables I and II, the relative intensity of the fragments formed by electron impact on the BF_3 remain constant to 1500°K. These data were obtained at a pressure of 10^{-6} torr (1 torr = 1 mm of Hg), corresponding to a flow rate of about 10^{15} molecules/sec.

The reaction of polycrystalline boron with fluorine in this apparatus confirms our earlier observation with ClF_3 as an oxidizer that the BF^+ intensity is greater than can be accounted for by electron bombardment of BF_3 (4b). Typical results for the reaction of fluorine and boron are given in Tables III and IV. A comparison of the relative intensities of BF^+ and BF_2^+ in Table IV with the normal cracking pattern of BF_3 (Table II) indicates that BF is the species evolved from the boron surface; this seems to eliminate BF_2 as a first-reaction product. The apparent low ratio of BF_2^+ to BF_3^+ results from a high background at mass number 68 (BF_3^+). This, of course, reduces the ratio of BF^+ to BF_3^+ also.

In order to relate the data obtained from the mass spectrometer to the surface reaction on the boron rod, the BF^+ intensity due to ionization of BF was obtained as the difference between the total BF^+ intensity and the BF^+ intensity resulting from the fragmentation of BF_3 in the mass spectrometer. The latter intensity was determined from the ratio of the mass 30 peak to the mass 49 peak in the normal spectrum of BF_3 . The actual magnitude for a given run is affected, along with other parameters, by the flow rate of fluorine and the position of the oxidant-inlet tube relative to the boron rod and the opening to the ion source of the mass spectrometer. Some of the variation in the BF^+ intensity from one run to another can be attributed to the difficulty of reproducing the same conditions with regard to these two variables in our present equipment.

Although a rate expression for the reaction of boron with fluorine can not be calculated from the data obtained to date because of apparent variations in the fluorine flow and the BF_3 background, some generalizations can be made:

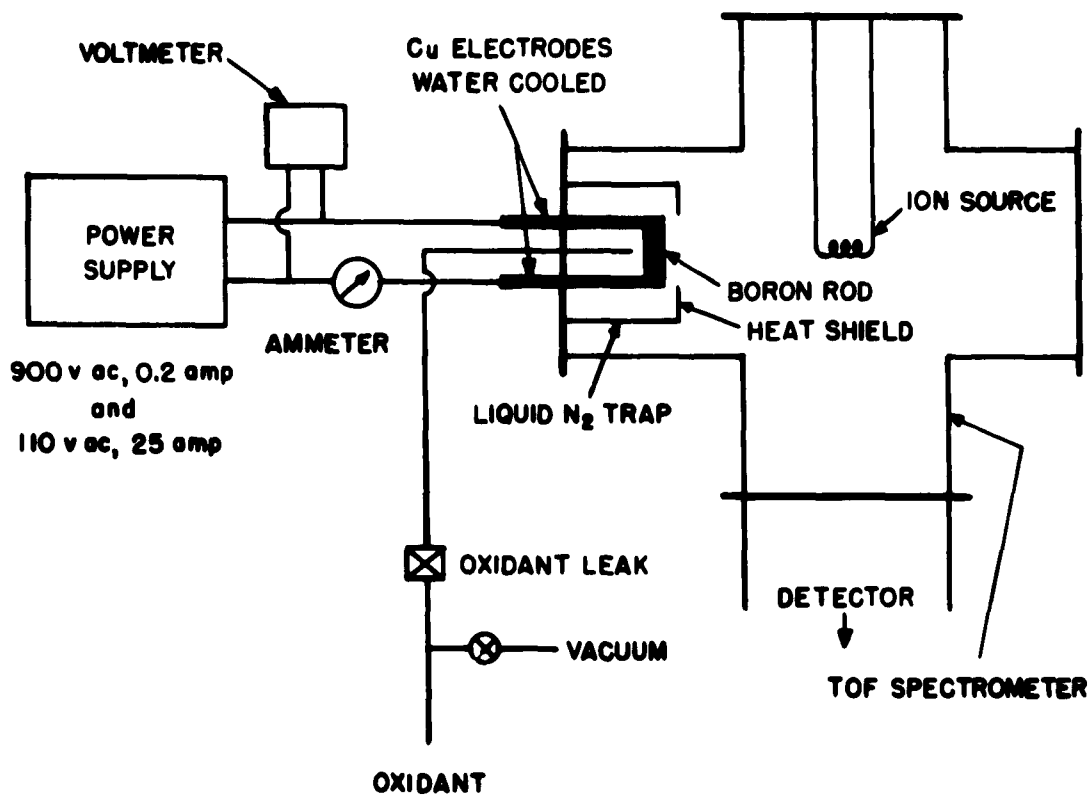


FIGURE I. SCHEMATIC DIAGRAM OF INLET SYSTEM FOR MASS SPECTROMETER

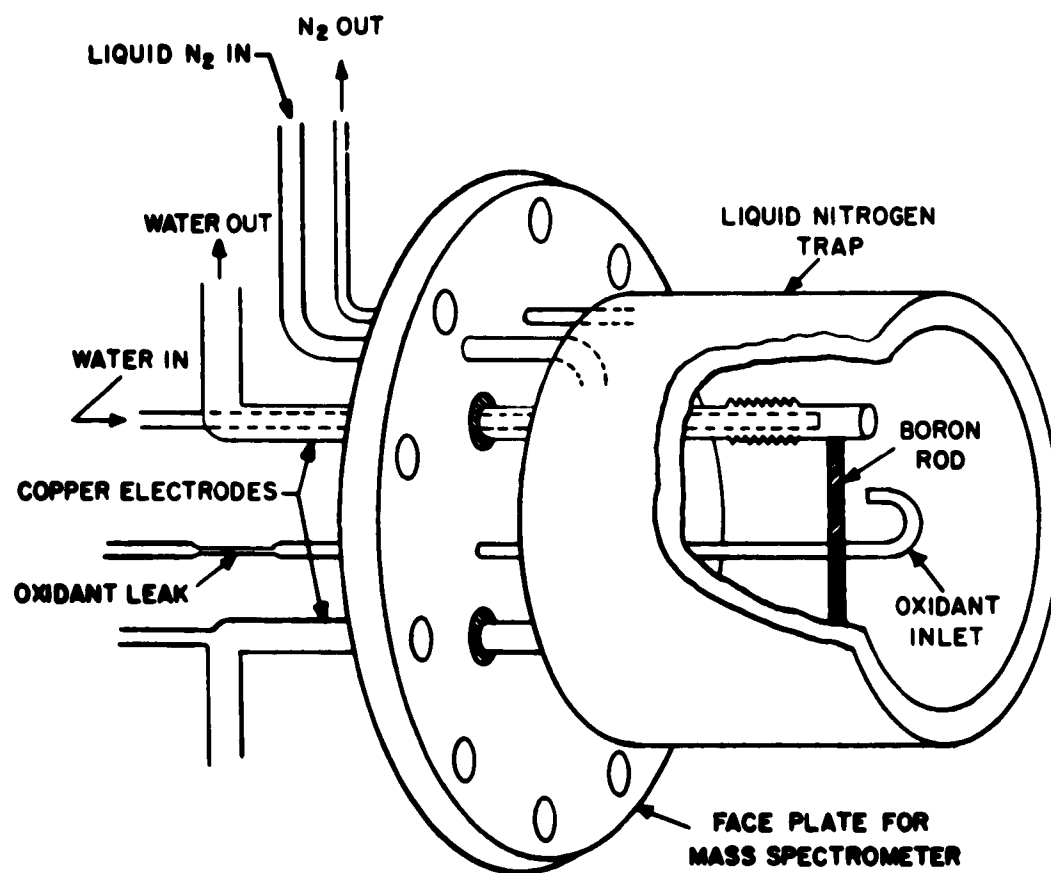


FIGURE 2. COMBUSTION APPARATUS FOR MASS SPECTROMETER

HEAT SHIELD REMOVED

TABLE I

INTENSITY (ARBITRARY UNITS) OF SPECTRAL PEAKS FOR BF₃

<u>m/e^a</u>	<u>Ambient</u>	<u>800^b</u>	<u>1060</u>	<u>1140</u>	<u>1250</u>	<u>1370</u>	<u>1470°K</u>
11 (B ⁺)	27.5	32.5	30.0	37.5	27.5	30.0	42.5
30 (BF ⁺)	20.0	25.0	25.0	29.5	20.0	25.0	30.0
48 (BF ₂ ⁺)	340	400	400	470	350	400	460
49 (BF ₂ ⁺)	1475	1750	1800	2000	1500	1700	2000
68 (BF ₃ ⁺)	97.5	110	110	125	95	105	125

^a Ratio of mass to charge.

^b Approximate.

TABLE II

RELATIVE INTENSITY OF SPECTRAL PEAKS FOR BF₃

	<u>Ambient</u>	<u>800^a</u>	<u>1060</u>	<u>1140</u>	<u>1250</u>	<u>1370</u>	<u>1470°K</u>	<u>A_v</u>
B ⁺ /BF ₃ ⁺	0.28	0.30	0.27	0.30	0.29	0.29	0.34 ^b	0.30
BF ⁺ /BF ₃ ⁺	0.21	0.23	0.23	0.24	0.21	0.24	0.24	0.23
BF ₂ ⁺ /BF ₃ ⁺	15.1	15.9	16.4	16.0	15.8	16.2	16.0	16.0

^a Approximate.

^b Probably high because of vapor pressure of boron.

TABLE III
INTENSITY (ARBITRARY UNITS) OF SPECTRAL PEAKS FOR REACTION
OF FLUORINE WITH A HEATED BORON ROD

<u>m/e^a</u>	<u>800^b</u>	<u>1120</u>	<u>1220</u>	<u>1400</u>	<u>1600</u>	<u>1650°K</u>
11 (B ⁺)	0.16	0.53	0.6	0.9	1.5	1.7
30 (BF ⁺)	2.8	4.6	5.7	7.0	10.5	10.0
49 (BF ₂ ⁺)	3.0	5.6	7.1	9.5	21.0	17.5
68 (BF ₃ ⁺)	0.30	0.44	0.60	0.62	1.4	1.3

^aRatio of mass to charge.

^bApproximate.

TABLE IV
RELATIVE INTENSITY OF SPECTRAL PEAKS FOR REACTION OF
FLUORINE WITH A HEATED BORON ROD

	<u>Run</u>	<u>800^a</u>	<u>1120</u>	<u>1220</u>	<u>1300</u>	<u>1400</u>	<u>1450</u>	<u>1500</u>	<u>1600</u>	<u>1650°K</u>
BF ⁺ /BF ₃ ⁺	1	3.3			15.2		14.0		14.0	2.5
	2	9.3	11.5	5.6		11.3			7.7	
	3		0.80	1.12	0.45			0.51		0.42
	4				0.70		0.42			0.36
	5		0.28		0.79		0.57			0.40
BF ₂ ⁺ /BF ₃ ⁺	1	15.			22.		22.		34.	46.
	2	10.	14.	12.		15.3			15.	
	3		15.8	11.3	12.7			17.3		16.4
	4				16.2			11.9		16.1
	5		16.7		16.1			10.2		12.6

^aApproximate.

- (a) The ratio $\text{BF}^+/\text{BF}_3^+$ is considerably greater than that expected from electron impact with BF_3 (Table IV).
- (b) The ratio $\text{BF}_2^+/\text{BF}_3^+$ is approximately equal to that due to electron impact on BF_3 (Table IV).
- (c) The BF_3^+ intensity increases with an increase in temperature and is apparently related to reactions on or desorption from surfaces other than the boron rod, such as the trap, radiation shield, and face plate.
- (d) The BF^+ intensity, generally, is only slightly dependent on temperature above 1200°K (Table V).

The last observation suggests the possibility of more than a single mechanism for the oxidation of boron with fluorine or of an activated desorption of BF from the boron surface.

MICROBALANCE EXPERIMENTS

The apparatus used to determine the rate of reaction of boron with fluorine is discussed in detail in reference 4b and is described only briefly here (see also Figure 3). The equipment consists of a high-purity polycrystalline boron rod suspended from a quartz helix inside a quartz reactor. Provision is made for admitting fluorine at low flow rates at pressures from 10^{-3} to 1 torr. The change in weight of the boron rod (approximately 3 mm in diameter and 26 mm long) is followed with a precision cathetometer. The rod is heated with an image furnace in which the filament of a 1000-w projection lamp operating at approximately 60 v is placed on the focal axis of one parabolic mirror and the boron rod on the axis of a similar mirror. The mirrors are formed by rolling a 4-by-6-inch metal sheet into the shape of a parabolic cylinder.

Experiments in which the boron rod at room temperature was exposed to fluorine gas at 1 to 200 μ Hg pressure for three to four hours gave no apparent change in the weight of the rod. However, with the boron rod approximately 600°K, a detectable weight change was observed. Figure 4 shows the experimental data for a typical run, and Table VI summarizes the results obtained at several pressures. The reaction rate appears to be more dependent on the flow rate of fluorine than on the pressure of fluorine. This would indicate that nearly all the fluorine reacted with the boron, a conclusion substantiated

TABLE V

BF⁺ INTENSITY (ARBITRARY UNITS) FOR REACTION OF
FLUORINE WITH HEATED BORON ROD

<u>Run</u>	<u>Ambient</u>	<u>800^a</u>	<u>1120</u>	<u>1220</u>	<u>1300</u>	<u>1400</u>	<u>1450</u>	<u>1500</u>	<u>1600</u>	<u>1650°K</u>
1		1.0			34.3		34.2		33.3	46.0
2		2.8	4.5	5.6		6.9			10.0	
3		0.7	2.7	3.4	3.8			3.9		3.4
4					16.6		16.4			10.9
5	0.2		0.7		7.8		10.8			9.7

^aApproximate.

TABLE VI

CONSUMPTION RATE OF BORON IN FLUORINE AT LOW PRESSURES
(PRELIMINARY DATA)

<u>Chamber Pressure, μ Hg</u>	<u>Flow Rate, molecules/sec</u>	<u>Reaction Rate, molecules B/cm²-sec</u>
150.	1.7 x 10 ¹⁷	2.8 x 10 ¹⁶
100.	2.0	3.2
73.	2.0	5.1
73.	1.3	2.7
5.	0.9	2.4
1.	0.6	1.6
0.8	0.9	1.9
0.8	0.6	1.0

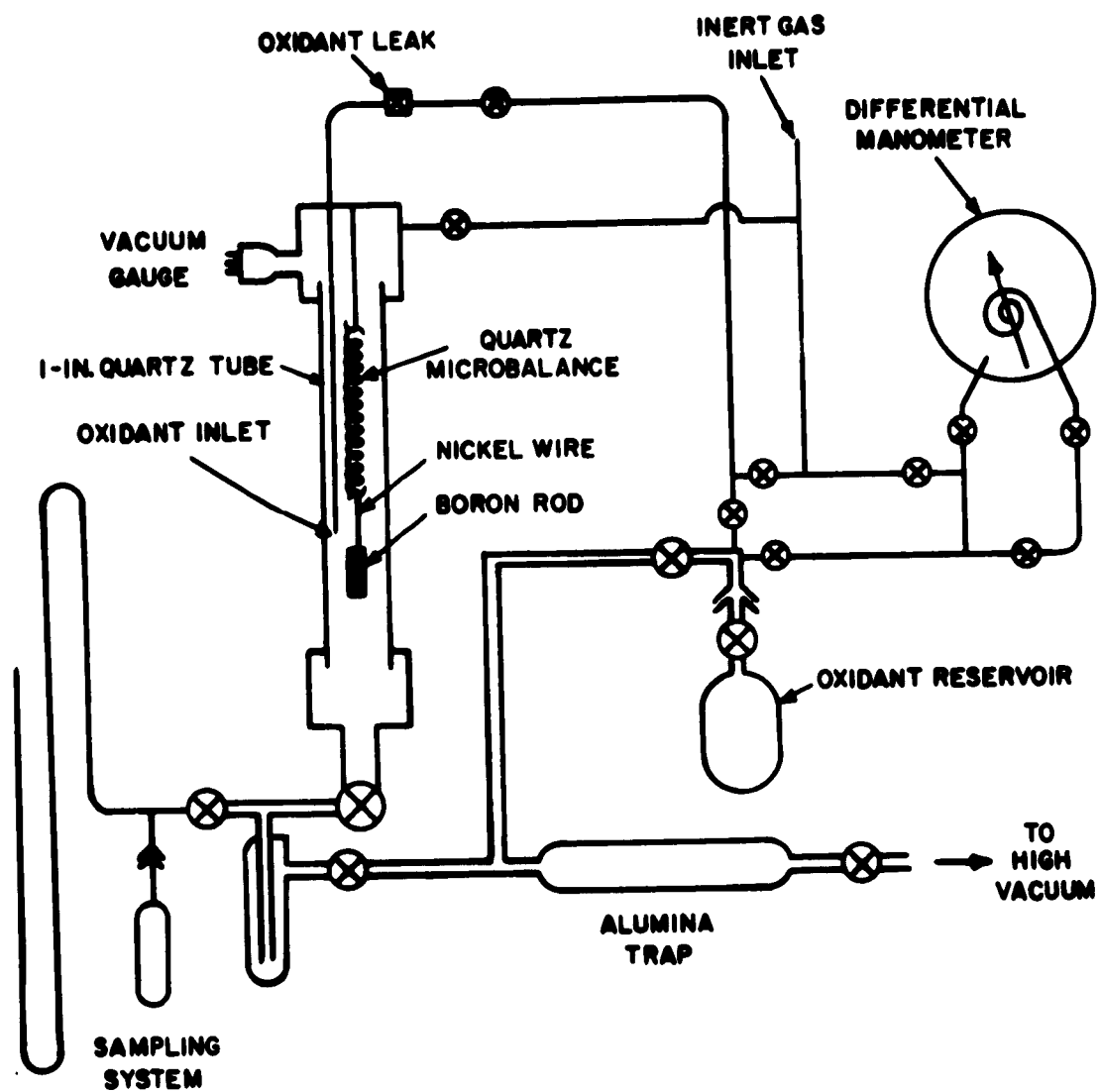


FIGURE 3. DIAGRAM OF COMBUSTION APPARATUS FOR KINETIC STUDIES

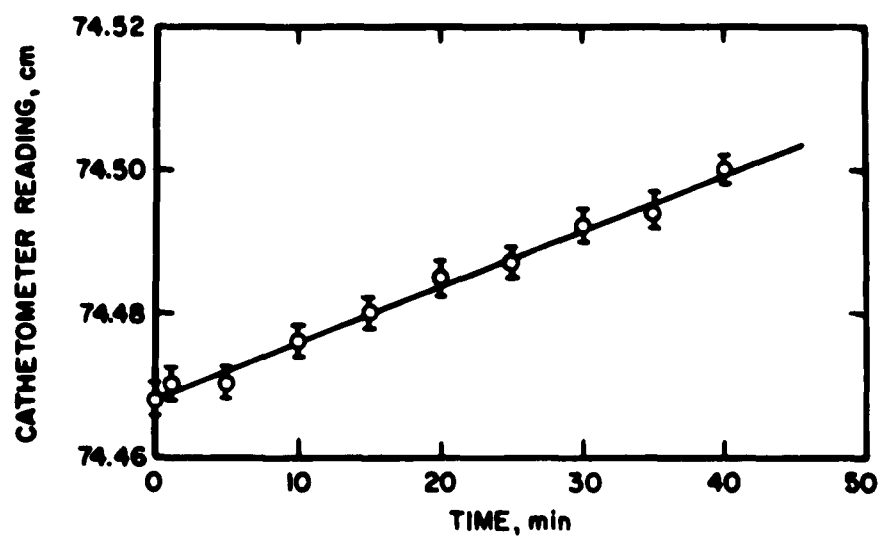


FIGURE 4. DECREASE IN LENGTH OF QUARTZ MICROBALANCE DURING REACTION OF BORON WITH FLUORINE GAS

by calculating a value of 5×10^{16} molecules/sec for the consumption of fluorine at 1μ (based on formation of BF_3) compared to a flow rate of 6×10^{16} molecules/sec. It is apparent from these preliminary experiments that the vacuum system will have to be modified to attain flow rates at which the reaction rate is independent of the flow.

FUTURE WORK

Experiments will be continued in the mass spectrometer and the microbalance apparatus. The mass-spectrometer experiments will be refined in an attempt to get reproducible ion intensities at various temperatures to determine the activation energy of the boron-fluorine surface reaction. An attempt will be made to modify the microbalance apparatus to conduct experiments at higher flow rates and permit the determination of the accommodation coefficient for the surface reaction.

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